

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-155201

(43)Date of publication of application : 28.05.2002

(51)Int.Cl.

C08L 71/02

C08L 27/08

C08L 33/06

C09K 3/10

(21)Application number : 2000-353206

(71)Applicant : ASAHI GLASS CO LTD

(22)Date of filing : 20.11.2000

(72)Inventor : WATABE TAKASHI
KASHIWAME KIYOTERU

(54) CURABLE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a curable composition not causing stringiness in use, having a small slump in an uncured state, excellent weather resistance for a long period of time after curing and a sufficiently high degree of lightening.

SOLUTION: This curable composition is characterized by comprising an oxyalkylene polymer containing a reactive silicon group represented by general formula (1) $-SiXaR1(3-a)...$ (1) [R1 is a monofunctional organic group; X is a hydroxy group or a hydrolyzable group; a is 1-3] and a polymer containing a (meth)acrylic acid alkyl ester monomer unit and minute hollow bodies of organic resin.

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CLAIMS

[Claim 1]

[Claim 1] An oxyalkylene polymer (A) which has a reactive silicon group expressed with a following general formula (I), and $-SiX_3R^{1'}(3-n) - (I)$

A univalent organic group of the carbon numbers 1-20 in which $R^{1'}$ may have a substituent, and X show a hydroxyl group or a hydrolytic basis among [type], and a shows an integer of 1-3, respectively. However, when $R^{1'}$ may be the same respectively or it may differ, when two or more $R^{1'}$ exist, and two or more X exists, X may be the same respectively or may differ.]

A hardenability constituent comprising

(Meta) A polymer (B) including an acrylic-acid-alkyl-ester monomeric unit.

An organic resin minute hollow body (C).

[Claim 2] The hardenability constituent according to claim 1, wherein said oxyalkylene polymers (A) are 6000 or more number average molecular weights and a 1.7 or less molecular weight distribution (Mw/Mn) oxyalkylene polymer.

[Claim 3] The hardenability constituent according to claim 1 or 2 being a polymer characterized by comprising the following.

A carbon number of an alkyl group of said polymer (B) is an acrylic-acid-alkyl-ester (meta)

monomeric unit of 1-8 as an acrylic-acid-alkyl-ester (meta) monomeric unit.

An acrylic-acid-alkyl-ester monomeric unit whose carbon number of an alkyl group is ten or more (meta).

[Claim 4] The hardenability constituent according to any one of claims 1 to 3 said polymer's (B's) is being a polymer including an acrylic-acid-alkyl-ester (meta) monomeric unit, and being a polymer whose resin minute hollow body (C) is a polyvinylidene fluoride resin minute hollow body (1).

[Claim 5] The hardenability constituent according to any one of claims 1 to 4, wherein said organic resin minute hollow body (C) is a polyvinylidene fluoride system resin minute hollow body.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0061] Field of the Invention This invention relates to a hygroscopic-surface-moisture hardening type hardenability constituent suitable as the main ingredients, such as sealant and adhesives, in more detail about a hardenability constituent.

[0002]

[Description of the Prior Art]The oxalkylene polymer which has reactive silicon groups, such as alkoxy silyl groups, (it is hereafter called a "hardened type oxalkylene polymer"). It can harden also at a room temperature with the hygroscopic surface moisture in the air, and since the hardened

material which has rubber elasticity is obtained and after hardening is excellent also in the adhesive property over various adherends, it is widely used as sealant, adhesives, base resin of the constituent

for covering / seal, etc.
[0003] However, when such a hygroscopic-surface-moisture hardening type oxyalkylene polymer is

a crack may arise on the hardened material surface, and improvement in weatherability is called for. [0004] As a method of raising the weatherability of a hardened type oxyalkylene polymer, for example, applied, for example to sealant, under the exposure condition in the outdoors, a white bluish mark and

the method indicated by JP.59-122541A, JP.60-31556A, JP.63-112642A, JP.6-172631A, etc. is known. According to these gazettes, it is supposed by making a hardened type

oxyalkylene polymer contain the acrylic acid-alkyl-ester system polymer which has a reactive silicon group (meta) that improvement in weatherability can be aimed at.

[0055] To the hardened type oxalkylene polymer containing the acrylic-acid-alkyl-ester system polymer which has a reactive silicon group (meta). The presentation which furthermore added bulking

agents, such as glass balloons, is indicated by JP, 5-86325, A.

weight:

[0008] [Problem(s) to be Solved by the Invention] However, when it used for the use of sealant, adhesives, etc. in addition to the presentation of an indication being still insufficient for JP-5-80325A in the presentation concerned as a coating agent for vehicles.

point of a weight saving, there was a problem that it was [that it is easy to produce a cobwebbing at the time of use] inferior to workability. When it was especially used for a joint part as sealant, there

was a problem that a slump (appet) was large.

and is a thing.
** does not occur, but the slump at the time of un-hardening is small, is excellent

also in

[0008]
One way for solving the problem is to use an excessive resin matrix hollow body as a bulking agent.

means for solving the problem by using an organic resin (instead of a barium salt) added to a hardened type oxalykene polymer containing an acrylic-acid-alkyl-ester system (polymer as a result of research) wholeheartedly that this invention person should attain the

polymer as a result of repeated loading or withdrawal from a liquid environment. The authors also noted that cobwebbing prevention which was not able to be attained reduction of a slump weatherability, and all the four characteristics of a slight saving could

2010/08/03

http://www.ipolnlpic.gov.jp/cgi-bin/ai_web_cg_cjcg:ainn_a-1map2004-2021

[illegible]

JP.2002-155201.A [DETAILED DESCRIPTION]

be attained in a presentation of an indication in the above-mentioned gazette, and this invention was completed.

[0009] Namely, an oxysilylene polymer (A) in which a hardenability constituent of this invention has a reactive silicon group expressed with a following general formula (1) and $-SiR^1$ (1).

whose characteristics, such as intensity after hardening of the hardenability constituent which the compatibility over the oxyalkylene polymer (A) of a polymer (B) improves, therefore is obtained. Improve by using such a combination as an acryloxy-acid-alkyl-ester monomer. As an acryloxy-acid-alkyl-ester monomer whose carbon number of an alkyl group is ten or more (meta). The acryloxy-acid-alkyl-ester (meta) monomer of 10-30 has a more preferred carbon number of an alkyl group, and the acryloxy-acid-alkyl-ester (meta) monomer of 10-22 has a still more preferred carbon number of an alkyl group.

[0046] The carbon number of an alkyl group as an acryloxy-acid-alkyl-ester (meta) monomer of 1-8. For example, methyl acrylate (meta), ethyl acrylate (meta), acryloxy acid (meta), propyl, butyl acrylate (meta), acryloxy acid (meta), hexyl, acryloxy acid (meta), octyl, 2-ethoxyethyl acrylate (meta), and acryloxy acid (meta), acryloxy acid (meta), decyl, acryloxy acid (meta), dodecyl, acryloxy acid (meta), and acryloxy acid (meta) are acryloxy-acid-alkyl-ester monomers whose carbon number of an alkyl group is ten or more (meta). For example, decyl acrylate (meta), acryloxy acid (meta), octadecyl, (Meta) Acrylic acid tetradecyl, acryloxy acid (meta) hexadecyl, acryloxy acid (meta) octadecyl, eicosanyl acrylate (meta), acryloxy acid (meta) docosa, n- and acryloxy acid (meta) hexacosyl are mentioned.

[0048] In the case where the carbon number of an alkyl group uses together the acryloxy-acid-alkyl-ester (meta) monomer of 1-8, and the acryloxy-acid-alkyl-ester monomer whose carbon number of an alkyl group is ten or more (meta). Although the ratio in particular is not restricted, as for the former/latter, it is preferred that it is 95 / 5 - 40/60 in a mass ratio, and it is more preferred that it is 95 / 5 - 40/60.

[0049] The polymer (B) in this invention may include unsaturation group content monomeric units other than the monomeric unit concerned other than an acryloxy-acid-alkyl-ester monomeric unit, as mentioned above (meta). (Meta) Although the compound expressed with the following general formula (10) is mentioned as unsaturation group content monomers other than an acryloxy-acid-alkyl-ester monomer, it is not limited to these.



R² shows the univalent organic group or hydrogen atom except an alkyl group among [type: R¹ is synonymous with said R²].

[0050] The univalent organic group except the alkyl group in a general formula (10) means the univalent organic group other than the alkyl group defined in a general formula (9). The univalent haals (for example, a hydrogen atom, a hydroxyl group, and polyalkylene glycol which have substituents (for example, a halogen atom, a hydroxyl group, an isopropenyl group, a phenoxy group, a furfuryl group, a reactive silicon group, etc.) other than a hydrocarbon group as such a univalent organic group are mentioned. As a compound expressed with a general formula (10), (Meta) Acrylic acid, Hydroxyethyl (Meta) Hydroxyethyl, such as acrylates, (Meta) Acrylate, isocyanateethyl (Meta) Isocyanateethyl, such as acrylates, (meta)-acrylate, (meta)-acrylate I, such as 2-phenoxylethyl (meta)-acrylate, 1 - furfuryl (hydrogen) acrylate, such as furfuryl (meta)-acrylate and tetrahydrofuran (meta)-acrylate. Have (Meta) Acrylate; gamma- (Methacryloxypropyl) Trimethoxysilane etc. (meta)-acryloxyalkyl alkoxyalane; - glycidyl (meta)-acrylate; - the acryloxy-ester (meta)- of polyalkylene oxide monomers, such as methoxy polyethylene-glycol (meta)-acrylate, etc. are mentioned.

[0051] (Meta) As an acryloxy-acid-alkyl-ester monomer and an unsaturation group content monomer which can be used together, a compound which was illustrated below besides what is expressed with the above-mentioned general formula (10) can be used. Namely, N-substitution or N,N-substitution (meta) acrylamide, such as N,N-dimethylacrylamide, Vinyl glycidyl ether, Unsaturated glycidyl ether, such as allyl glycidyl ether and methyl glycidyl ether, Crotonic acid glycidyl, (Nonalkyl) monoglycidyl ether or diglycidyl ether of glycidyl ester, unsaturated decarboxylic acid of unsaturation monocarboxylic acid, such as dimaleic acid glycidyl and vinylmaleic acid glycidyl, Styrene, Styrene monomers, such as 2-vinyl-6-bromo hexanoic acid, 2-vinyl-6-bromo hexanoic acid glycidyl, (meta)-acryloxyalkyl ether, halogenated alkyl, halogenated ester, vinyl ether, such as vinyl halogenated, isopropenyl ether, chloroacrylate, etc. can be used.

[0052] The manufacturing method in particular of the polymer (B) in this invention is not restricted. (Meta) It can polymerize by a radical polymerization, anionic polymerization, cationic polymerization,

etc., using the above-mentioned unsaturation group content monomer which uses an acryloxy-acid-alkyl-ester monomer as an essential ingredient. In this invention, as for a polymer (B), polymerizing an radical polymerization may be preferred, and the gels may be any of solution polymerization, an emulsion polymerization, suspension polymerization, and bulk polymerization.

[0053] When carrying out a radical polymerization, a radical polymerization initiator is usually added as a radical source of release to the above-mentioned unsaturation group content monomer. As a radical polymerization initiator which can be used in this invention, the polymerization initiator radical compound (initiator) such as azobisisobutyronitrile, azobisisobutyronitrile, azobisisobutyronitrile, 2,2'-azobis (2-amidinopropane) dihydrochloride, 2,2'-azobis (2-amidinopropane) dihydrochloride, 2,2'-azobis (2-amidinopropane) dihydrochloride, benzoyl peroxide, t-butyl peroxide, acetyl peroxide, diisopropyl peroxide, diisobutyl peroxide, etc. can be illustrated. When activated with radiation or heat, a radical polymerization initiator is not necessarily required. It is preferred to perform the above-mentioned reaction at 20-200 °C (preferably 50-150 °C) for several hours - tens hours.

[0054] When compounding a polymer (B) by a radical polymerization in this invention, it is the purposes, such as molecular weight control, and a chain transfer agent may be added. As a chain transfer agent, alkyl mercaptan, such as n-dodecyl mercaptan, t-dodecyl mercaptan, and n-butyl mercaptan, an alpha-methylstyrene dimer, etc. can be used.

[0055] A polymer (B) may polymerize under the nonexistence of the hardenability constituent ingredient of this invention other than a polymer (B), or may polymerize under a polymer (B) polymerizing under existence of hardenability constituent ingredients other than a polymer (B). Polymerizing under existence of an oxyalkylene polymer (A) is preferred. By polymerizing a polymer (B) under existence of an oxyalkylene polymer (A), mixed time and effort can be saved and the dispersibility of the polymer (B) in an oxyalkylene polymer (A) can also be raised. It is also considered that a part of unsaturation group content monomer for polymers (B) carries out graft polymerization in the middle of a polymerization at an oxyalkylene polymer (A), in such a case, a graft polymerization thing functions as a compatibilizer and the dispersibility of a polymer (B) improves more. [0056] In this invention, it is preferred to use a polymer (B) as a polymer including an acryloxy-acid-alkyl-ester monomer unit mentioned above, and it is a polymer which has a reactive silicon group connected with the following general formula (11).



R¹, R², X, and a among [type: X]

[0057] When a polymer (B) has a reactive silicon group expressed with the above-mentioned general formula (11), in particular the number and the existence part of a reactive silicon group in the molecule of a polymer (B) are not restricted. The number of a reactive silicon group is just one or more, and the end or side chain of a polymer (B) molecule may be sufficient as an existence part, or they may be both end and a side chain.

[0058] As a method of introducing the reactive silicon group expressed with the above-mentioned general formula (11), following (a) - the method of (N) are mentioned to a polymer (B). The method of the following (a) - (N) may be combined and may be performed. (a) How to use together the unsaturation group content monomer which has a reactive silicon group expressed with a general formula (11) in polymerizing an unsaturation group content monomer. (b) How to use the initiator which has a reactive silicon group expressed with a general formula (11) in polymerizing an unsaturation group content monomer. (c) How to use the initiator which has a reactive silicon group expressed with a general formula (11) in polymerizing an unsaturation group content monomer.

[0059] A method to which the compound which has a reactive silicon group which is polymerizing an unsaturation group content monomer which uses together the unsaturation group content monomer which has a specific functional group, and is expressed with the specific functional group concerned, a reactant basis, and a general formula (1) is made to react.

[0059B] The compound which is used in the method of the above-mentioned (b) and which is expressed with the following general formula (11) as an unsaturation group content monomer which has a reactive silicon group expressed with a general formula (1) is preferred.



R⁶ shows among [type the univalent organic group which has an unsaturation group. R¹, X, and a are

days under 60% of humidity at 20 °C, the 5-mm-thick hardened material was made to form on said aluminum plate, and this was made into the specimen. The exposure examination was done for this specimen with the Suga Test Instruments Co., Ltd. make sunshine super long life weather meter, and the surface state of the specimen of 1000 hours, 1500 hours, and 1800 hours after was observed, to which, as for the standard of evaluation, neither Omikinas nor a crack is accepted and to which a white bluish mark and a crack are accepted a little [*2]: It was presupposed that the white bluish mark and crack which were carried out clearly are accepted.

[0112] Next, applied the constituent of Example 1 and the comparative examples 1-2 on the aluminum plate of 1-mm thickness so that it might be set to 0.2 mm in thickness, and recuperated oneself for seven days under 60% of humidity at 20 °C, the 0.2-mm-thick hardened material was made to form on said aluminum plate, and this was made into the specimen. The exposure examination was done for this specimen with the Suga Test Instruments Co., Ltd. make sunshine super long life weather meter, and the surface state of the specimen of 1000 hours, 1500 hours, and 1800 hours after was observed.

The standard of evaluation was that it is the same as that of the above.

[0113] The specimens 1-2 at the time of sending the constituent of Example 1 and the comparative examples 1-2 with the state where it does not harden, by a spatula was observed, and workability was evaluated. The standard of evaluation was made into Obwebbing nothing and those with cobwebbing. Based on JIS A1439, the vertical mold specimen estimated the slump (mm) at 50 mm using the constituent of Example 1 in the state where it does not harden, and the comparative examples 1-2. The specific gravity of the constituent (after hardening) of Example 1 and the comparative examples 1-2, was measured based on the A method of JIS K7112.

[0114] The result of the above-mentioned examination is summarized in the following table 2, and is shown. When thickness was thick (thickness: 5 mm), also in any when thickness is thin (thickness: 0.2 mm), the constituent obtained by Example 1 and the comparative examples 1-2 showed good weatherability, so that clearly from the result shown in Table 2. However, as for the hardenability constituent of Example 1, a cobwebbing was not accepted to the cobwebbing having been seen by the evaluation test of workability as for the hardenability constituent of the comparative examples 1 and 2.

[0115] In the hardenability constituent of Example 1, a lapset was not observed to the lapset having produced the hardenability constituent of the comparative examples 1 and 2 in the slump test. In the hardenability constituent of Example 1, although the amount of the minute hollow body (organic resin minute hollow body) used was 0.6 copy to 100 copies of Pa, low specific gravity constituent resin less than 14.8% rather than the specific gravity of the constituent of the comparative examples 1 and 2, the constituent (comparative example 2), but in spite of being mixed fine copies of glass balloons for the hardenability constituent of the comparative examples 1 and 2, the constituent of Example 1 made 1 to 100 copies of Pa as a minute hollow body. The reduction ratio of the specific gravity from an unadded hollow body hardenability constituent (comparative example 2) was only 5.8%.

[Table 2]

試験の 結果	試験例		
	1	2	3
試験の 結果	1000時間 1500時間 1800時間	0 0 0	0 0 0
試験の 結果	300時間 600時間 900時間	0 0 0	0 0 0
加工後 (へら取れ性)	0	0	0
スランプ(mm)	0	2	5
硬化物の比重	1.21	1.34	1.42

[0117]

[Table 3]

番号	化学種
*1	硬質塩化アルミニウム系硬化剤 (硬化促進剤)
*2	有機系硬化剤 (硬化促進剤)
*3	硬化促進剤 (硬化促進剤)
*4	硬化促進剤 (硬化促進剤)
*5	硬化促進剤 (硬化促進剤)
*6	硬化促進剤 (硬化促進剤)
*7	硬化促進剤 (硬化促進剤)
*8	硬化促進剤 (硬化促進剤)
*9	硬化促進剤 (硬化促進剤)
*10	硬化促進剤 (硬化促進剤)
*11	硬化促進剤 (硬化促進剤)
*12	硬化促進剤 (硬化促進剤)

[0118]

[Effect of the Invention] As explained above, according to this invention, a cobwebbing does not occur at the time of use, but the slump at the time of un-hardening is small, the weatherability over the long period of time after hardening is also excellent, and it also enables the degree of a weight saving to provide a hardenability constituent high enough further.

[Translation done.]